REMARKS

Claims 1- 30 are in the case.

Applicants thank the Examiner for the courtesy extended to Applicants' representative at several telephonic communications for the parent application 09/300,544 conducted in January, February and March, 2002 following the Advisory Actions.

Claims 1, 14, 20, 22, 28 and 30 have been amended. Support for the amendment to the claims can be found in the original disclosure, e.g., at page 5, lines 25-26; page 10, line 29; page 12, line 1; page 9, line 7 to page 10, line 3; original claims and examples. A marked-up version of the changes made to the claims by the amendment is attached. The attached pages are captioned "**Version with Markings to Show Changes Made**."

Applicants submit that entry of this preliminary amendment together with the following remarks, which addresses all the issues raised in the final Office Action mailed on November 6, 2001, the Advisory Action mailed on January 11, 2002, the Advisory Action mailed on February 6, 2002, and the Advisory Action mailed on March 13, 2002 during the prosecution of the parent application 09/300,544, is believed to place the application in condition for allowance. Favorable consideration of the subject application in view of the preliminary amendment and the remarks is respectfully requested.

I. Rejection of Claims 1-30 under 35 U.S.C. 102 (b) over Alper et al

On pages 2-3 of the final Office Action mailed on November 6, 2001, the previous claims 1-30 were rejected under 35 U.S.C. 102 (b) over US 5,149,741 to Alper et al. (hereafter "Alper").

Applicants respectfully traverse the rejection because Alper fails to teach or suggest a hot melt adhesive composition including unconventionally less amount of substantially aliphatic high Tg tackifying resin than that of the thermoplastic base polymer, as recited in the independent claims 1, 20 and 30. Alper also fails to teach or suggest a hot melt adhesive composition including a thermoplastic base polymer selected from the group consisting of copolymers and terpolymers of ethylene, amorphous polyalphaolefins, homogenous ethylene/α-olefin interpolymer, and mixtures thereof, as recited in the independent claims 20, 22 and 28.

Independent claims 1, 20, 22, 28 and 30 have been amended to clarify these important aspects of the invention.

As addressed in the specification, both heat resistance and cold temperature resistance are important properties for hot melt adhesives. It has been a problem to improve both properties simultaneously as one is improved at the cost of the other. Using higher amount of tackifying resin(s) improves high heat resistance, which, however, would adversely affect cold temperature resistance. Using higher amount of the thermoplastic base polymer improves cold temperature resistance, which, on the other hand, would adversely affect heat resistance. (specification, page 2, paragraph 2).

Surprisingly, the subject invention has resolved the problem by selecting substantially aliphatic tackifying resins with high glass transition temperature (Tg) and by combining unconventionally lower amount of the selected high Tg tackifying resin(s) with higher amount of the thermoplastic base polymer. In doing so, the claimed adhesive exhibits significantly improved heat resistance at no cost of cold temperature resistance. (specification, page 5, lines 8-14).

A). **Independent Claims 1 and 30**

Each of the independent claims 1 and 30 is directed to a hot melt adhesive composition that requires, among other things, that the substantially aliphatic high Tg tackifying resin(s) concentration is less than the thermoplastic base polymer concentration. The thermoplastic base polymer is described, e.g., on page 10, line 29 and page 12, line 1 of the specification, and would be well understood by person skilled in the art upon reading the specification.

Alper discloses, in general, a hot melt adhesive composition including, among other things, 15 to 40 parts by weight of a styrene-isoprene-styrene (SIS) block copolymer, and 40 to 70 parts by weight of a compatible tackifying resin. (col. 4, lines 4-15). Alper teaches that SIS block copolymer is a base polymer (col. 1, lines 27-30; col. 2, lines 30-49; col. 3, lines 10-20). Alper teaches, in general, that at least equal or more amount of tackifying resin is used relative to that of the base polymer (SIS block copolymer).

However, Alper fails to teach that less amount of tackifying resin is used relative to that of the base polymer (SIS block copolymer). Particularly, Alper fails to teach that substantially aliphatic high Tg tackifying resin is used in less amount relative to that of the base polymer (SIS block copolymer).

Example 2 of Alper is not to the contrary. Alper specifies in Example 2 an adhesive composition including, among other things, 35 parts base polymer (SIS block copolymer), 40 parts tackifying resin (Escorez 5340, a hydrogenated dicyclopentadiene resin). Clearly, the exemplified amount (40 parts) of the tackifying resin is more than the exemplified amount (35 parts) of the base polymer (SIS block copolymer).

At least for that reason, Alper does not and cannot anticipate claims 1 and 30.

There have been arguments during the prosecution of the parent application 09/300,544 as to whether the "aromatic reinforcing resin (Endex 155 from Hercules Inc.)" in example 2 of Alper should be considered as a base polymer, thus, should be added to the thermoplastic base polymer concentration. Applicants submit that the aromatic reinforcing resin of Alper is not a thermoplastic base polymer because it has been clearly categorized as a tackifying or modifying resin. Therefore, it should not be included in the thermoplastic base polymer concentration.

Applicants submit herewith a copy of "Resins for Elastomer-Based Adhesives", J. S. Autenrieth and K. F. Foley, the Handbook of Adhesives, edited by Irving Skeist, 3rd ed., pp. 556-568, 1990 as Exhibit A, which explains in more detail about tackifying or modifying resins including endblock reinforcing resins e.g., aromatic reinforcing resin used in Alper. For example, "Strictly speaking, all resins added to an adhesive formulation modify the properties of that system and thus would be considered modifying resins…" (*Id.* p. 561, emphasis added). "with the development of block copolymer-based pressure sensitive adhesives, another class of resin, the endblock reinforcing resin, has come into widespread use. These resins associate only with the styreneic blocks of the copolymers and increase the shear resistance of the adhesive formulation." (*Id.* p. 561, emphasis added). In Table 1, Endex® series, one of which--Endex 155-- is used in Example 2 of Alper, is listed as reinforcing resin under broader modifying resins category. (*Id.* p. 564). In Table 3, endblock reinforcing resins (C)--high soften point aromatic resins-- are listed as modifying resins for block copolymers. (*Id.* p. 568).

Moreover, the Hercules attachment submitted on August 23, 2001 together with the response to the first Office Action mailed on May 30, 2001 is also consistent with the above-cited publication. Hercules lists Endex ® 155, the aromatic reinforcing resin used in Example 2 of Alper, under the term "resin", e.g., under "Endex ® Resins" and "the Hercules Spectrum of Hydrocarbon Resin". Under "Endex ® Resins", Hercules further describes, "The specific molecular weight and solubility of these resins make them particularly suited to reinforce the styrenic domains of block copolymers in hot melt and pressure sensitive adhesive applications." (emphasis added). The listing and description of Hercules, therefore, are also consistent with the category and descriptions of the endblock reinforcing resins in the above Exhibit A. That is, the aromatic reinforcing resin in Example 2 of Alper--Endex ® 155--is not a base polymer, but a modifying resin.

Further, Applicants submit herewith a copy of "Adhesive, Sealants and Coatings Manual", Quantum Chemical Corporation, USI Division, pp. 10, 11, 14 and 17 as Exhibit B, which explains the differences between a polymer (i.e., a base polymer) and a tackifying resin in hot melt adhesives. For example, "a typical hot melt adhesive is composed of three components: polymer, tackifying resin, and wax." "The polymer forms the backbone of the adhesive, controlling its strength and toughness." "The backbone polymer is normally modified with a low molecular weight, non-crystalline, polymeric material known as tackifying resin." (*Id.* p. 11, emphasis added). "The polymer is the single most important component of a hot melt adhesive..." (*Id.* p. 14). "The tackifier improves the adhesion characteristics of the polymer." (*Id.* p.17).

Throughout the "Adhesive, Sealants and Coatings Manual", the term "polymer" is used referring to the base polymer--the backbone of the adhesive, but not to any types of

polymeric materials. Likewise, the term “resin” or “tackifying resin” is used referring to certain polymeric materials having a low molecular weight and functioning as a modifier to improve the adhesion characteristics of the base polymer.

As evidenced by Exhibit B and also well known to persons skilled in the relevant art, the term “polymer” has been used specifically as a synonym of “base polymer” in hot melt adhesive industry. This is also apparent from Alper. Alper uses the term “polymer” or “copolymer” for the base polymers (Alper, col. 1, line 27-col. 2, line 55), and the term “resin”, such as “tackifying resin”, “endblock reinforcing resins”, “aromatic reinforcing resin”, etc. for non-base-polymer materials or resins added to the adhesive composition to improve the properties of the base polymer. (Alper, col. 3, lines 20-27; col. 7, lines 1-48).

As claims 1 and 30 have been clearly defined that the substantially aliphatic high Tg tackifying resin concentration is less than the thermoplastic base polymer concentration. There is no doubt that Alper fails to teach at least that aspect of claims 1 and 30. Alper also fails to even remotely suggest the combination of such a high Tg tackifying resin with such a less amount as already discussed above. Therefore, Alper does not and cannot anticipate claims 1 and 30.

B). <u>Independent Claims 20, 22 and 28</u>

Each of independent claims 20, 22 and 28 is directed to a hot melt adhesive composition that requires including, among other things, at least one thermoplastic base polymer selected from the group consisting of copolymers and terpolymers of ethylene; amorphous polyalphaolefins, homogenous ethylene/α-olefin interpolymer, and mixtures thereof.

Alper teaches an adhesive composition including only a styrene-isoprene-styrene (SIS) block copolymer as base polymer. Evidently, Alper fails to teach an adhesive composition including at least one thermoplastic base polymer selected from copolymers and terpolymers of ethylene, amorphous polyalphaolefins, homogenous ethylene/α-olefin interpolymer, and mixtures thereof. Alper also fails to even remotely suggest the combination of substantially aliphatic high Tg tackifying resin with the above selected thermoplastic base polymer.

At least for these reasons, Alper does not and cannot anticipate claims 20, 22 and 28.

All the dependent claims also cannot be anticipated, *inter alia*, by Alper for the reasons delineated above, because each of them is directed to a combination including everything recited in the corresponding independent claim.

Accordingly, Applicants submit that the rejection of previous claims 1-30 under 35 U.S.C. 102 (b) over Alper has been overcome and request that it be withdrawn.

II. Rejection of Claims 1-30 under 35 U.S.C. 103 (a) over Alper et al

The previous claims 1-30 were also rejected, in the alternative, under 35 U.S.C. 103(a) over US 5,149,741 to Alper et al. (hereafter "Alper") as stated on pages 3-4 of the final Office Action mailed on November 6, 2001. Especially, the claims are rendered *prima facie* obvious due to alleged lack of showing unexpected results.

As already discussed in more detail above, Alper fails to teach or suggest the selection of the high Tg tackifying resin. Alper provides a laundry list of all kinds of tackifying resins (Alper, col. 7, lines 1-44), but in nowhere Alper teaches or suggests to

select substantially aliphatic tackifying resins having Tg of greater than about 65°C to improve heat resistance.

In contrast, the subject invention has selected substantially aliphatic tackifying resins having Tg of greater than about 65°C, which, in combination with the other aspects of the invention, has achieved significantly improved high heat resistance. As show by the examples, e.g., on Table III, the adhesive of Example 7 including a substantially aliphatic tackifying resin having a Tg of 81°C exhibits bond failure at 87°C (about 188.6 °F). On the other hand, Comparative Examples C, D and E, each including a tackifying resin having a Tg of no greater than about 65°C, exhibit bond failure at much lower temperatures--57° C (about 134.6° F), 52 °C (about 125.6 °F), and 32° C (about 89.6° F), respectively. The similar results are obtained in Example 6 and Comparative Examples A and B when using different base polymer. (Specification, page 24, Table III)

Further, Alper fails to teach or suggest the use of lower tackifying resin concentration relative to the base polymer concentration in combination with the selected high Tg tackifying resin to improve heat resistance. Alper teaches, in general, that at least equal or more amount of tackifying resin is used relative to that of the base polymer. Alper particularly teaches much higher amounts of tackifying resins in all the examples. Especially, the amounts of the tackifying resins can be as high as 60 parts relative to 25 parts base polymer in ten out of twelve examples. In doing so, all the tested adhesives exhibit bond failure (i.e., complete delamination) at a temperature of 100°F (about 38°C). (Alper, col. 13, line 11-28; Tables I and II). In addition, Alper uses bond retention at 120°F (about 49°C) to express elevated temperature resistance of his adhesives. *(Id.* col. 15, line 67 to col. 16, line 48). As shown by all the examples, none of the tested adhesives

retain 100% bond at 120°F (about 49°C) after bonding for 4 hours, i.e., none of the tested adhesives survive the temperature of 120°F(about 49°C). Some of the adhesives only retain 38 % bond at 120°F (about 49°C) after 4 hours. (*Id.* Tables I and II).

In contrast, the claimed adhesives including less substantial aliphatic high Tg tackifying resin concentration relative to the base polymer concentration do not exhibit failure or delamination at the temperature of 100°F (38°C) or 120°F (about 49°C), which are the desired temperatures of Alper. Instead, the claimed adhesives show significantly improved heat resistance, as expressed by 100g Peel temperature. (100g Peel temperature is the temperature at which the adhesive composition exhibits failure--delamination). As shown by examples, the adhesives including less high Tg tackifying resin concentration than the base polymer concentration exhibit bond failure at much higher temperatures relative to Alper's. For example, in Example 2, an adhesive including 40 wt% ethylene vinyl acetate (EVA) base polymer and 30wt% high Tg tackifying resin exhibits failure at 60°C (140°F). In Examples 3 and 4, by using different amounts of EVA base polymer and high Tg tackifying resin, the adhesives exhibit failure at 67°C (152.6°F) and 68°C (154.4°F), respectively. In examples 6 and 7, 100g Peel temperature can be as high as 81°C (177.8°F) and 87°C (188.6°F), respectively. (Specification, example 2; Tables I and III).

Further, Alper fails to teach or suggest the use of any base polymer other than SIS block copolymer. Alper does not even remotely teach or suggest the use of a base polymer selected from copolymer and terpolymers of ethylene, copolymers and terpolymers of ethylene, amorphous polyalphaolefins, homogeneous ethylene/a-olefin

interpolymers, and mixtures thereof, and in combination with high Tg tackifying resin(s) to improve heat resistance.

Alper specifically addresses several problems associated with the use of ethylene vinyl acetate copolymers (EVA) and amorphous polypropylene (APP) as base polymer in formulating hot melt adhesives. The first problem is that "they lacked the desired elevated temperature resistance." (Alper, col. 1, lines 30-37). The desired elevated temperature, according to Alper, is 100°F (38°C). (*Id.* col. 1, lines 38-45). Due to this and other problems with EVA and APP base polymers, Alper clearly states, "Those skilled in the art will recognize that adhesives based upon EVA or APP <u>cannot</u> generally be formulated as multi-purpose adhesive composition." (*Id.* col. 1, lines 53-55, emphasis added). Thus, Alper teaches to formulate adhesives using, instead, SIS block copolymer as base polymer. (*Id.* col. 4, lines 4-8). Obviously, Alper teaches to formulate adhesives <u>without</u> using ethylene vinyl acetate (EVA) or amorphous polypropylene (APP), because EVA and APP lack the desired heat resistance to the desired elevated temperature, which is 100°F (38°C).

In contrast, in the subject invention, the claimed adhesive composition includes a thermoplastic base polymer selected from copolymer and terpolymers of ethylene, amorphous polyalphaolefins, homogeneous ethylene/a-olefin interpolymers, and mixtures thereof. Surprisingly, the claimed adhesives including the above selected base polymers, when combined with the high Tg tackifying resin(s), exhibit significantly improved heat resistance to much higher temperature than the desired elevated temperature of Alper -- 100°F (38°C). For example, Table I shows that adhesives including ethylene vinyl acetate base polymer exhibit 100g Peel temperature of 152.6°F (67°C) and 154.4°F (68°C),

respectively. Table II shows that adhesive including an ethylene/1-octene interpolymer exhibits 100g Peel temperature of 172.4°F (77°C). Further, Table III shows that 100g Peel temperature of Example 7 can be as high as 188.6°F (87°C) when using ethylene-propylene copolymer. (Specification, Tables I, II and III).

Undoubtedly, the chemically different adhesive compositions of the subject invention as well as the unique properties would not be obvious to persons skilled in the art following the teachings of Alper.

Moreover, Alper does not provide any desirability of modifying his high level of tackifying resin to a low level such that the tackifying resin concentration would be less than the base polymer concentration. Nor does Alper teach the selection and the use of substantially aliphatic high Tg tackifying resins when doing so. Evidently, by teaching to formulate composition with higher amount of the tackifying resin relative to that of base polymer, Alper teaches away from the claimed invention.

Furthermore, Alper does not provide any desirability of substituting his SIS block copolymer for a thermoplastic base polymer selected from copolymers and terpolymers of ethylene, amorphous polyalphaolefins, homogeneous ethylene/a-olefin interpolymers, and mixtures thereof. Nor does Alper provide any suggestion or motivation of combining substantially aliphatic high Tg tackifying resin with the above selected base polymer. By teaching to formulate composition that cannot use ethylene vinyl acetate (EVA) or amorphous propylene (APP), etc., Alper, again, teaches away from the claimed invention, and teaching away is "strong evidence of nonobviousness." *In re Hedges*, 783 F.2d 1038, 1041, 228 USPQ 685, 687 (Fed. Cir. 1986).

If it is not shown that the prior art gives a reason or motivation to make the claimed compositions, then there is no *prima facie* case and the applicant should prevail. *In re Grabiak*, 769 f.2d 729 (Fed. Cir. 1985). Such an argument does not require the applicant to make a showing of new or unanticipated results. *Id.*

Although not required, evidence in the specification, as already discussed in detail above, does demonstrate that the claimed compositions exhibit unexpected results relative to that of Alper.

As stated above, traditionally, higher heat resistance is generally achieved using higher amounts of tackifying resins such as, in fact, taught by Alper. Alper uses much higher concentrations of tackifying resin(s), yet the composition exhibits bond failure at much lower temperature--only 100ºF (about 38ºC).

In contrast and surprisingly, the claimed adhesive compositions exhibit unexpected high heat resistance. By using unconventionally lower amount of substantially aliphatic high Tg tackifying resin(s), the claimed adhesives exhibit bond failure at much higher temperatures, e.g., as high as 87ºC (188.6ºF). The superior properties provided by the subject invention would not be obvious to persons skilled in the art upon reviewing the disclosure of Alper. Thus, the unexpected advantages and superior properties offered by the subject invention provide further evidence that the subject invention is not obvious over Alper.

In view of all the forgoing, claims 1-30 is not obvious over Alper.

Accordingly, Applicants submit that the rejection of previous claims 1-30, in the alternative, under 35 U.S.C. 103 (a) over Alper has been overcome and request that it be withdrawn.

In light of the above amendment and remarks, Applicants respectfully submit that all the rejections made in the Office Action mailed on November 6, 2001 and the follow-up Advisory Actions have been overcome, therefore, should be withdrawn.

Respectfully submitted,

Date: 04/01/02

Bin Su

Bin Su, Pro. Reg. No. P-51,309

H.B. FULLER COMPANY
Patent Department
P.O. Box 64683
St. Paul, MN 55164-0683
Tel: (651) 236-5502
Fax: (651) 236-5126

VERSION WITH MARKINGS TO SHOW CHANGES MADE

In the Specification:

Paragraph at line 7 of page 1, has been amended as follows:

This application [is a Continuation-In-Part] claims the priority of U.S. provisional patent application serial no. 60/091,231 filed June 30, 1998.

In the Claims:

Claims 1, 14, 20, 22, 28 and 30 have been amended as follows:

1. (Three time amended) A hot melt adhesive composition comprising:

a) about 10% by weight to about 50% by weight of at least one substantially aliphatic tackifying resin having a glass transition temperature of greater than 65°C;

b) about 20% by weight to about 60% by weight of at least one thermoplastic base polymer; and

c) 0% by weight to about 40% by weight of at least one wax;

wherein said [total] tackifying resin concentration [having a glass transition temperature of greater than 65°C] is less than said [total] thermoplastic base polymer concentration.

14. (amended) The adhesive of claim 1 wherein said at least one thermoplastic base polymer is a copolymer of ethylene, [wherein] at least one comonomer of said

copolymer [is] being selected from the group consisting of vinyl acetate, n-butyl acrylate, methyl acrylate, vinyl esters and mixtures thereof.

20. (Three time amended) A hot melt adhesive composition comprising:

a) about 10% by weight to about 50% by weight of at least one tackifying resin having a glass transition temperature of at least 65°C;

b) about 20% by weight to about 60% by weight of at least one thermoplastic base polymer selected from the group consisting of copolymers and terpolymers of ethylene; amorphous polyalphaolefins, homogenous ethylene/α-olefin interpolymer, and mixtures thereof; and

c) 0% by weight to about 40% by weight of at least one wax;

wherein said [total] tackifying resin concentration [having a glass transition temperature of at least 65°C] is less than said [total] thermoplastic base polymer concentration.

22. (Twice amended) A hot melt adhesive composition comprising:

a) about 10% by weight to about 50% by weight of at least one hydrocarbon tackifying resin derived, at least in part, from dicyclopentadiene and having a glass transition temperature of greater than about 65°C;

b) about 10% by weight to about 80% by weight of at least one thermoplastic base polymer selected from the group consisting of copolymers and

terpolymers of ethylene; amorphous polyalphaolefins, homogenous ethylene/α-olefin interpolymer, and mixtures thereof; and

28. (Twice amended) A hot melt adhesive comprising:

a) from about 10% by weight to about 80% by weight of at least one aliphatic tackifying resin having a [T_g] glass transition temperature (T_g) of greater than 65°C; and

b) from about 10% by weight to about 80% by weight of at least one thermoplastic base polymer selected from the group consisting of copolymers and terpolymers of ethylene; amorphous polyalphaolefins, [rubbery block copolymers] homogenous ethylene/α-olefin interpolymer, and mixtures thereof.

30. (Twice amended) A hot melt adhesive composition comprising:

a) about 10% by weight to about 50% by weight of at least one substantially aliphatic tackifying resin having a softening point of greater than 140°C;

b) about 20% by weight to about 60% by weight of at least one thermoplastic base polymer; and

d) 0% by weight to about 40% by weight of at least one wax;

wherein said [total] tackifying resin concentration [having a softening temperature of greater than 140°C] is less than said [total] thermoplastic base polymer concentration.

HANDBOOK OF ADHESIVES
Third Edition

Edited by

Irving Skeist, Ph.D.

Consultant to the Polymer Industries
Skeist Incorporated
Whippany, New Jersey

VNR VAN NOSTRAND REINHOLD
New York

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Resins for Elastomer-Based Adhesives

JOHN S. AUTENRIETH
Hercules Incorporated
Retired
and
KENDALL F. FOLEY
Hercules Incorporated
Wilmington, Delaware

Elastomer-based adhesives are widely used in industrial and household applications. Pressure sensitive tapes and labels, hot melt packaging adhesives, disposable products, construction adhesives, and hot melt bookbinding adhesives are just a few of the adhesive systems which have shown rapid market growth in recent years. Other types of elastomer-based adhesives have been developed for high-strength structural applications required by the aircraft, automotive, and construction industries. The wide range of properties available in these adhesive systems is due in part to: (a) the variety of properties obtainable in natural and synthetic elastomers and (b) the many modifying materials such as tackifying resins, reinforcing resins, fillers, plasticizers, and curing agents which may be incorporated into the adhesive formulation.

HISTORICAL BACKGROUND

The earliest rubber adhesives were merely simple solutions of unmodified natural rubber. The adhesive properties of raw natural rubber were recognized as long ago as 1791, when naphtha solutions of rubber were used for laminating and waterproofing textile products. Later, such adhesives were vulcanized after application. Adhesives made with natural rubber latex were first prepared in the middle of the 19th Century. The early solvent cements were seldom formulated with resins, although the inclusion of rosin was found to be beneficial. Strength requirements in these early adhesives were, for the most part, low.

With the development of synthetic elastomers during World War II, new types of adhesives appeared for application to a broader range of substrates and for use at higher temperatures. Styrene-butadiene and butadiene-acrylonitrile copolymers found application in new adhesives. There were also significant concurrent developments in adhesives based on chlorinated rubber, polychloroprene (neoprene), and polysulfide rubber. Development of carboxylic elastomers, silicone rubbers, and polyurethanes followed.

The introduction of a number of elastomer-thermosetting resin blends extended the application of elastomer-based adhesives to structural applications. These blends typically

consisted of reactive phenolic resins with neoprene or nitrile rubber. The key properties of these adhesives were high strength and low creep.

The commercial introduction of the thermoplastic block copolymers in 1965 gave impetus to the development of high performance pressure sensitive and hot melt adhesives. These unique materials, based on styrene endblocks and either isoprene, butadiene, or ethylene-butylene midblocks, have become established as the elastomer of choice in some of the fastest growing segments of the adhesive and sealant industry.

ADHESIVE COMPONENTS

Elastomer-based adhesives typically contain an elastomer and a tackifying or modifying resin as key components. A number of other ingredients may be included:

1. Elastomer.
2. Tackifying (modifying) resin.
3. Plasticizer or softener.
4. Fillers.
5. Pigments.
6. Curing agents.
7. Antioxidants.

An elastomer is a natural or synthetic polymer with rubberlike properties. These materials exhibit high extensibility and quick, forceful recovery. Examples of elastomers used in adhesive applications are:

- Natural rubber.
- Acrylic copolymers.
- Styrenic block copolymers.
- Butyl rubber.
- Chlorinated rubber.
- Polyisobutylene.
- Styrene-butadiene rubber (SBT).
- Polychloroprene (neoprene).
- Silicone rubber.
- Ethylene-propylene copolymer rubber.
- Polyurethanes.
- EPDM.

The tackifying (or modifying) resins which are used in formulating elastomer-based adhesives are obtained by the polymerization of petroleum and terpene feedstreams, as well as from the derivatization of wood, gum, and tall oil rosin. These are low molecular weight resins, with the Mw seldom exceeding 2000 and often below 1000. In addition, thermoplastic and thermosetting phenolic resins are often incorporated into high performance adhesives. Tackifying resins comprise the subject matter for most of this chapter and will be discussed in detail later.

Plasticizers and softeners include the phthalates such as dioctyl phthalate and diisobutyl phthalate, natural oils such as lanolin, and paraffin, naphthenic and aromatic oils obtained from petroleum refining. Liquid resins from rosin or petroleum feedstocks can serve the dual purpose of tackification and plasticization.

Fillers are materials such as carbon black, zinc oxide, clays, chalk, whitings, calcium silicate, and barium sulfate. These materials are used to reduce cost, increase hardness, improve abrasion resistance, and to modify the cohesive strength of the formulation.

Curing agents are incorporated into the adhesive formulation to increase the cohesive strength of the elastomer. Sulfur was the most commonly used curing agent in early natural rubber adhesive systems, but it has been largely replaced by organic peroxides and isocyanate crosslinking systems.

The antioxidants used in adhesive formulations are similar to those used in rubber compounding and include materials such as the aromatic amines, substituted phenols, and hydroquinoes. Elastomer and resin manufacturers typically incorporate antioxidants (0.1–0.3 wt %) in their products for protection during storage and shipment. Adhesive formulators will usually add additional antioxidant to protect the adhesive during processing and use. It is not unusual for an adhesive formulation to contain as many as three or four different types of antioxidants.

In addition to the components cited above, aqueous adhesives based on rubber latexes and resin emulsions also employ a wide variety of materials, such as protective colloids, emulsifiers, thickeners, and emulsion stabilizers. The primary function of these additives is to provide stability to the aqueous adhesive. They do not necessarily enhance the adhesive properties of the finished composition. In fact, a careful

compromise must be reached between the dispersion properties and the performance characteristics of the adhesive. Migration of stabilizers can reduce the tack of pressure sensitive adhesives upon aging or can cause staining of backing substrates. Improper use of stabilizers in latex adhesives can also result in poor resistance to moisture in the final application.

TYPES OF ELASTOMER-BASED ADHESIVES

Pressure sensitive adhesives based on a variety of elastomers and applied from either latex, solvent, or hot melt systems have shown rapid growth in recent years. In addition, the development of hot melt assembly adhesives based on the styrenic thermoplastic elastomers is a key factor in the production of disposable diapers and other sanitary products. Even though the current emphasis of elastomer-based adhesive development is on pressure sensitive adhesives, large volumes of solvent cements, latex cements, and mastics are still produced.

Solvent Cements

The preparation of many solvent cements, mastics, and pressure sensitive adhesives involves milling or mastication of natural rubber. The elastomer, obtained by the coagulation of natural rubber latex, is usually kneaded by passing repeatedly between two steel rolls moving at different speeds or in a Banbury-type mixer, usually at an elevated temperature. The polymer is subjected to compression followed by strong shearing forces. The very high shearing force mechanically ruptures the elastomer chains, thus reducing the molecular weight of the rubber. Whereas the starting material was essentially elastic and capable of undergoing permanent deformation only under extreme loads, after milling, it becomes softer, readily deformable, and soluble in both aliphatic and aromatic solvents.

In practice, it is difficult to define and control rubber milling conditions. The concentration and type of natural products in raw natural rubber vary, as do the amount and type of materials in the synthetic rubbers. These variables influence the result of mastication. The milling operation itself is one of skill and art. Temperature, speed of rolls, surrounding atmosphere, time of milling, and clearance between the rolls are all variables which are difficult to duplicate, not only from machine to machine, but for each batch operation on the same machine. The ability to mill to the same level of degradation is essential to obtaining a consistent cohesive strength in the adhesive formulation. Differences in milling levels become especially apparent in the shear resistance of natural rubber pressure sensitive adhesive unless the cohesive strength is regenerated by curing of the adhesive.

The measurement of the effects of mastication on the molecular weight of the rubber can be time-consuming even with sophisticated techniques such as size exclusion chromatography. The viscosity of natural rubber is usually measured by means of a Mooney rotating disk viscometer,[1] an established method for following the effect of mill time and conditions. Adhesive formulators have successfully used this instrument to correlate Mooney viscosity to rubber end-use properties.

Solvent cements are generally produced by removing the milled elastomer from the mill and dissolving it in solvent. This "cutting" of the rubber into a solvent is accomplished in low-speed mixing equipment known as *churns* or in a variety of high-speed, heavy-duty mixers. For natural rubber and SBR, solvents such as toluene, hexane, or naphtha are commonly used. For nitrile, neoprene, and other polar polymers, polar solvents such as methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), or chlorinated solvents may be used, alone or in blends with the nonpolar solvents. The blend of solvents finally used by the adhesive producer will depend not only on solvent power, but on the relative rates of evaporation which control drying time. The dissolved rubber can then be blended with whatever additives are needed to obtain the desired adhesive performance.

The process of masticating and dissolving natural rubber is important for pressure sensitive formulation as well as for solvent cement production. Pressure sensitive tapes and labels based on natural rubber are a significant part of the rapidly growing pressure sensitive adhesive

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Solvent cements are usually supplied at concentrations of 10–25% solids, with viscosities in the range of 1,000–30,000 cPs. They may be applied by brush, spray, doctor blade, reverse-roll coater, hand roller, trowel, and many other application methods. The proper coating of the adhesive is obtained by establishing the correct viscosity for the particular application method. After application, the solvent is removed by ambient drying or by forced drying in heated ovens or tunnels.

Solvent cements encompass a wide range of performance properties, from the simple natural rubber based cements which are widely used for low performance applications in homes and schools to the structural applications of contact adhesives based on polychloroprene and reactive phenolic resins.

Latex Adhesives

A rubber latex is a two-phase system consisting of particles of rubber dispersed in water. Protective colloids and other stabilizing agents will be present in a latex to keep the rubber well dispersed and to prevent agglomeration or coagulation of the rubber particles. Natural rubber is collected as a latex from certain species of tropical trees, in particular, *Hevea brasiliensis*. The rubber particles exist as globules of 1–3 microns diameter at a solids level of 35–40%.

A number of synthetic rubbers are produced by emulsion polymerization and are, therefore, available in latex form. Those of greatest commercial interest are SBR, acrylic, neoprene, and vinyl acetate–ethylene. Rubber latexes, particularly natural and SBR, have been used for many years in carpet and upholstery backsizings, bag, shoe, and bookbinding adhesives, tile mastics, tire cord dips, and wookworking adhesives.

Environmental concerns, which have resulted in restrictions on the use of organic solvents, have been the impetus for a strong interest in the use of rubber latexes in the formulation of pressure sensitive tapes and labels, can sealants, and contact adhesives. The availability of suitable rubber latexes and tackifying resin dispersions have made this change possible, and pressure sensitive adhesives based on natural rubber, SBR, and acrylic latexes have become a significant part of the adhesive industry. The production of tackifying resin dispersions will be discussed in more detail later in this chapter.

Latex adhesives offer several advantages over solvent systems. In addition to being more environmentally acceptable, latex systems offer minimum fire hazards, easy cleanup of equipment, and higher solids content. A rubber latex is considerably less viscous at much higher solids content than a corresponding solvent system.

Natural rubber latex at 40% solids is much lower in viscosity than a 15% solids solution of milled rubber in toluene. In addition, the natural rubber in latex form is of much higher molecular weight than the milled rubber. This higher molecular weight yields much higher shear resistance when formulated into pressure sensitive adhesives.

A key aspect of formulating latex adhesives with rubber and resins is the compatibility of the individual latexes. Dispersing agents may be cationic, nonionic, or anionic. Knowledge of the chemical nature of the systems is critical to preventing coagulation of the solids when blending a rubber and a resin latex.

While solvent cements may provide greater ultimate strength than latex systems, the latter types find wide use and are often necessary for certain bonding requirements. Solvent systems penetrate into a porous substrate, with the result that multiple applications are often necessary to put enough adhesive on the surface to form a satisfactory bond. Since latex systems exhibite better "hold-out" on porous surfaces, one coat of such an adhesive is often sufficient for good bonding.

Mastics

Mastics constitute a special type of adhesive which may be either latex or solvent-based. The unique characteristic of mastics is their extremely high viscosity. Most mastics contain natural rubber, SBR, or a blend. Some asphalt or bitumen may be added to lower raw material cost. Tackifiers and fillers are widely used.

Mastics are used in large volume, chiefly in

industrial applications and in the construction industry, where low bond strengths are adequate. They are used to install vinyl, rubber, or wood floor tiles, ceiling and ceramic wall tiles, vinyl and linoleum sheets, indoor-outdoor carpeting, and in the automotive industry for fastening insulation, silencer, and lining pads.

A simple latex mastic for applying ceramic tiles and wood flooring can be made by adding a high solids solution (> 80% solids) of an appropriate tackifying resin to an SBR latex with sufficient agitation to disperse the resin in the latex. Fillers may also be used in such a formulation. Such a mastic would then be applied to the floor or wall by trowel. The tile to be bonded is applied immediately with pressure before a skin forms on the mastic.

Pressure Sensitive Adhesives

Pressure sensitive adhesives constitute the fastest growing segment of the rubber-based adhesive industry. A variety of pressure sensitive tapes and labels are available, such as:

- Tapes:
  - Packaging.
  - Medical.
  - Masking.
  - Office/consumer.
- Labels:
  - Permanent.
  - Removable.
  - Low temperature/freezer grade.
  - Film and foil.

Pressure sensitive adhesives, unlike cements or hot melt packaging adhesives, are formulated to remain permanently tacky at the application use temperature. The challenge to formulate such products has been met by the development of specially designed tackifying resins and polymers. Such adhesives are characterized by rapid adhesion to the bonding surface. By the proper choice of polymer and resins, the adhesion characteristics can be varied to give permanent or removable adhesives as well as adhesives which show either adhesive or cohesive failure upon peeling. These formulating principles will be discussed in more detail in the section on tackifying resins.

The first commercial applications of pressure sensitive tape were in surgical tape and in friction tape for electrical, plumbing, and similar fastening applications. These were typically cloth-backed tapes which did not necessarily strip cleanly from the contacted surface. Later developments yielded general purpose masking tapes for household use and high-temperature resistant masking tapes for automotive painting applications. Polypropylene film-backed packaging tapes constitute a significant portion of the pressure sensitive tape industry today.

Pressure sensitive tapes and labels are offered with a variety of backing materials such as crepe paper, aluminum foil, fabric, cellophane, kraft paper, cellulose acetate, polyester film, polyethylene, polypropylene, plasticized poly(vinyl chloride), woven glass fiber cloth, or other flexible materials. Pressure sensitive adhesives may be applied from solvent, latex, hot melt, or radiation cured 100% solids systems. A wide variety of coating methods are utilized such as roll coating, calendering, slot die, and transfer coating.

A key factor in the growth of pressure sensitive adhesives has been the development of elastomers specially designed for pressure sensitive applications. Natural rubber is an important elastomer in these applications, as are carboxylated SBR latexes and solvent and latex acrylic. The thermoplastic block copolymers based on styrene endblocks and a rubbery midblock of isoprene, butadiene, or ethylene-butylene, and the styrene-butadiene multiblock copolymers have become established as the elastomers of choice in some of the fastest growing segments of the pressure sensitive adhesive industry. These highly stable and versatile materials offer a combination of properties which permit the formulation of high-performance adhesive systems. The unique molecular block structure of these copolymers offers special challenges to the adhesive formulator, and these will be discussed in more detail in the section on tackifying resins.

Hot Melt Adhesives

The class of adhesives applied in hot melt form has become a significant part of the adhesive industry in recent years. The environmental

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pressures on solvent based adhesives which has given impetus to latex adhesives have also given increased impetus to developing suitable hot melt systems. A key reason for the growth of hot melt adhesives has been the development of more thermally and oxidatively stable modifying resins and elastomers.

These thermoplastic hot melt adhesives are composed of 100% solids nonvolatile materials, i.e., containing no water, solvents, etc. They are solid at room temperature, but melt and flow readily at application temperature, 275–350°F. After application, bonding and cooling, hot melt adhesives return to a solid state and develop their ultimate strength.

The early hot melt adhesives were not strictly definable as rubber-based adhesives. Most "rubber" polymers such as natural rubber and random SBR are of such molecular weight and structure that they do not melt readily to a workable coating consistency at a temperature below which thermal degradation and decomposition take place. Certain synthetic polymers, however, lend themselves to the formulation of a wide range of hot melt adhesive compositions. Polyamide and polyester resins, ethylene-vinyl acetate (EVA) copolymers, ethylene-ethyl acrylate (EEA) copolymers, low molecular weight polyethylene and amorphous polypropylene, and certain vinyl ethers have found application in hot melt adhesives. These adhesives have found wide use in packaging, industrial, and construction applications.

The commercialization of the styrenic triblock copolymers in 1965 and the introduction of the styrene butadiene multiblock copolymers in the early 1980s have caused an increased interest in the application of hot melt adhesives. Not only have these materials greatly expanded the applications of hot melts into product assembly such as disposable diapers and other sanitary products, but the ability to formulate hot melt pressure sensitive adhesives from these copolymers has been a boon to the pressure sensitive adhesive industry. Hot melt pressure sensitive adhesives are ideally suited where fast production speeds, relatively low raw material cost, and the elimination of the need to remove or recover solvent are essential to the favorable economics of the manufacturing process.

FUNCTION OF RESINS IN ELASTOMER-BASED ADHESIVES

Resin Typ s

In the formulation of early elastomer-based adhesives, it was soon learned that a simple system consisting of natural rubber alone gave only marginal performance as a finished adhesive. Most commercially available synthetic elastomers have little tack, either to themselves or to other surfaces. Modifiers were found to contribute improvement in the adhesive performance characteristics.

Tackifying and modifying resins are represented by a variety of products of many different chemical types and physical properties. To a new adhesive formulator, the array of resins offered must seem bewildering and the choice of an appropriate resin must seem to be nothing more than mix and test. There is, however, a body of knowledge concerning elastomers and resins which allows for a systematic approach to the selection of the best modifying resin for a particular system. This systematic approach will be discussed in more detail shortly.

The first point of confusion concerns the terminology of tackifying vs. modifying resins. Strictly speaking, all resins added to an adhesive formulation modify the properties of that system and thus would be considered modifying resins. The majority of resins are added to an elastomer to generate increased tack or adhesion properties and are, thus, correctly called tackifying resins. Resins used in EVA, polyethylene, or other non-pressure sensitive hot melt adhesives are incorporated primarily to modify the viscosity and control open time. Thus, they are more correctly called modifying resins. With the development of block copolymer-based pressure sensitive adhesives, another class of resin, the endblock reinforcing resin, has come into widespread use. These resins associate only with the styreneic blocks of the copolymers and increase the shear resistance of the adhesive formulation.

Modifying resins have the following characteristics:

1. Low molecular weight, thermoplastic polymers (Mw 200–2000);
2. Viscous liquids to hard, brittle glasses at room temperature;

3. Obtained from the derivatization of rosin or by the polymerization of petroleum distillates, turpentine fractions, coal tar, and pure monomers;
4. Range from water-clear to dark brown or black in color; and
5. Are soluble in aliphatic and aromatic hydrocarbons as well as in many other common organic liquids.

The general classes of resins, based on their chemical nature, are:

1. Rosin, modified rosin, and rosin derivatives;
2. Hydrocarbon resins; and
3. Terpene resins.

Rosin resins are produced from the three types of rosin—gum, tall oil, and wood. Fig. 1 shows the sources and processing steps used to obtain rosin from pinewood.

Although unmodified rosin has some application in low quality mastics and construction adhesives, rosin is typically modified to enhance its oxidative and thermal stability and to obtain a range of physical properties such as softening point and melt viscosity. Rosin is a complex mixture of tricyclic unsaturated resin acids with some nonacidic components. At least

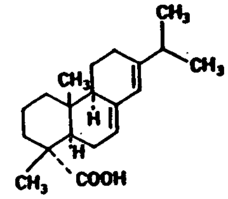

Fig. 2. Abietic acid.

twelve resin acids have been identified. Abietic acid, Fig. 2, is a common resin acid.

The derivatization of rosin focuses on the carboxyl group and the double bonds. Double bond reactions such as isomerization, hydrogenation, dehydrogenation, polymerization, and Diels-Alder adduction are typically carried out. Reactions of the carboxyl group include salt formation, esterification, hydrogenolysis, ammonolysis, and decarboxylation. Fig. 3 is a schematic or rosin derivatization carried out by one manufacturer, Hercules Inc.

Hydrocarbon resins are typically classified by the chemical nature of the feedstreams used, i.e., aliphatic, aromatic, cycloaliphatic, or mixed aliphatic-aromatic feedstreams. The main classes of resins commercially available are:

1. Aliphatic resins (C-5);
2. Aromatic resins (C-9);

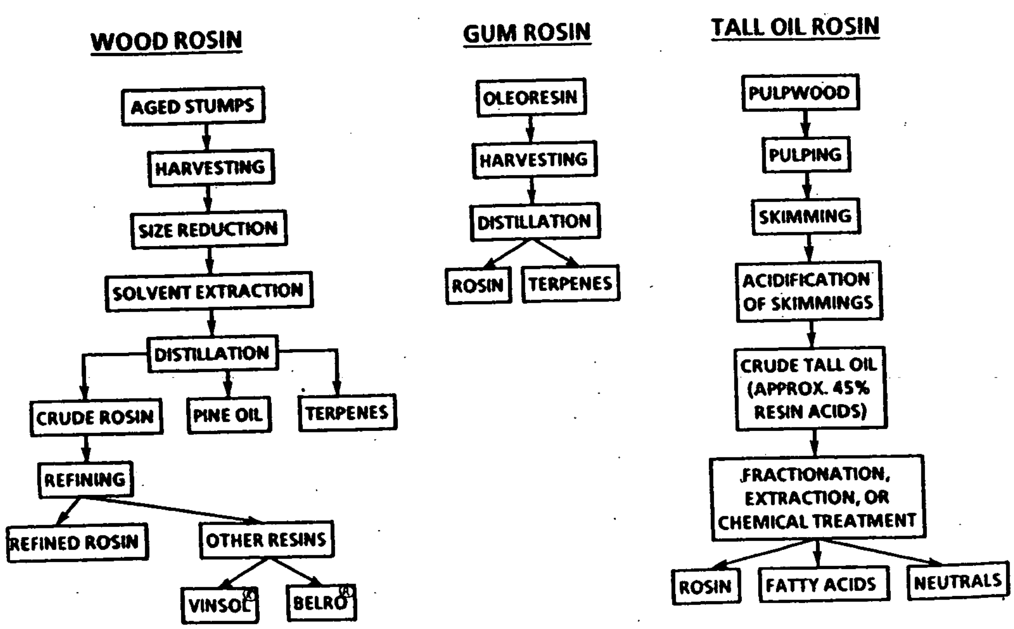

Fig. 1. Sources of rosin from pine wood.

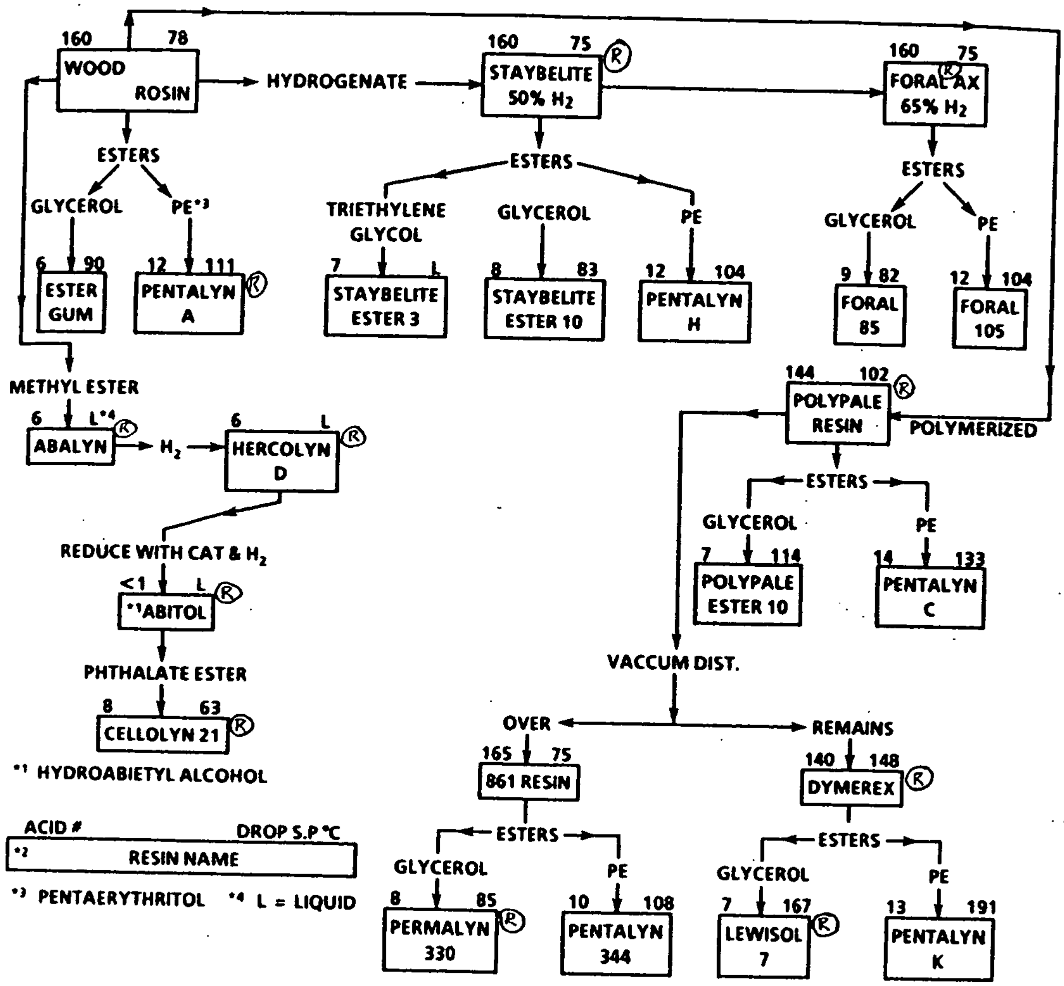

Fig. 3. Hercules, Inc., rosin derivatization.

3. Aromatic/aliphatic resins (C-5/C-9);
4. Pure monomer resins based on styrene, alphamethylstyrene (AMS), and vinyltoluene; and
5. Hydrogenated resins.

Polyterpene resins, aromatic-modified terpene resins, and phenolic-modified terpenes are produced from alpha-pinene, beta-pinene, *d*-limonene, and dipentene. Examples of the various resins listed by chemical type, trade name, physical properties, and manufacturer are found in Table 1.

Tack

Before discussing the function and selection of resins for adhesives, some discussion of tack and adhesion is necessary. To produce a suitable adhesive, three key criteria are required:

1. Tack or wetting properties;
2. Adhesive strength; and
3. Cohesive strength.

Tack is a term that is difficult to define in specific terms. Tack frequently represents a combination of many physical properties. Measurement of tack by application of finger pressure, a common technique, is obviously not quantitative. In adhesives technology, tack may be defined as the property of a material which enables it to form a bond of measurable strength immediately upon contact with another surface, usually with low applied pressure. Tack is thus "instantaneous" adhesion and differs

Table 1. Modifying R sins—Typ s and Properti s.

Resin Type	Trade Name	Acid No.	Softening Point, °C Drop[a]	R&B[b]	Manufacturer
Rosins:					
Gum rosin		165		78	China, Brazil
Tall oil rosin		163		80	5, 6
Wood rosin	Pexite®	160	80	73	1
Modified Rosins:					
Polymerized rosin	Poly-pale resin	144	102	95	1
Hydrogenated rosin	Staybelite	160	76	68	1
Disproportionated rosin	Dymerex resin	140	148		1
Rosin Esters:					
Pentaerythritol–wood rosin	Pentalyn A	12	111		1
Glycerine–hydrogenated wood rosin	Staybelite Ester 10	8	83		1
Pentaerythritol–hydrogenated wood rosin	Pentalyn H	12	104		1
Glycerine–highly hydrogenated wood rosin	Foral 85	9	82		1
Pentaerythritol–stabilized rosin	Pentalyn 344	10	104		1
Hydrocarbon Resins:					
Aliphatic petroleum	Piccotac® series	0		70–115	1
	Escorez® series	0		90–115	2
	Wingtack® series	0		86–115	3
Aromatic petroleum	Piccovar® series	0		10–60	1
	Picco® 5000 series	0		70–140	1
	Nevchem® series	0		70–150	4
Dicyclopentadiene	Piccodiene® 2215	0		115	1
Heat reactive	Neville® LX series	0		90–155	4
Aromatic modified aliphatic	Hercotac® 1149	0		96	1
	Super Sta-Tac®	0		80–100	7
Polymerized Terpenes:					
Alpha-pinene	Piccolyte® A series	0		115–135	1
d-Limonene	Piccolyte C series	0		10–135	1
Beta-pinene	Piccolyte S series	0		10–135	1
Aromatic modified	Zonatac® 105	0		105	5
Terpene phenolic	Nirez® 2000 series	0		122–148	7
Polyterpene	Nirez 1000 series	0		10–135	7
Pure Monomer Resins:					
Styrene/AMS	Kristalex® series	0		25–140	1
AMS/vinyl toluene	Piccotex® series	0		75–120	1
Styrene	Piccolastic® series	0		5–75	1
Hydrogenated Hydrocarbon:					
Cycloaliphatic	Regalrez® series	0		18–138	1
	Escorez 5000 series	0		80–120	2
	Super Nirez series	0		100–120	7
	Regalite® series	0		70–120	1
Reinforcing Resins					
	Endex® series	0		155–160	1
	Kristalex 5140	0		140	1
	Cumar® Lx-509	0		155	4

[a]Hercules drop softening point
[b]ASTM Method E28-67 Ring & Ball method

Manufacturers:
1. Hercules Inc.
2. Exxon Chemical Co.
3. Goodyear Chemicals.
4. Neville Chemical Co.
5. Arizona Chemical Co.
6. Union Camp Corp.
7. Reichhold Chemicals, Inc.

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· Point,

R&B[b]	Manufacturer
78	China, Brazil
80	5, 6
73	1
95	1
68	1
	1
	1
	1
	1
	1
	1
70–115	1
90–115	2
86–115	3
10–60	1
70–140	1
70–150	4
115	1
90–155	4
96	1
80–100	7
115–135	1
10–135	1
10–135	1
105	5
122–148	7
10–135	7
25–140	1
75–120	1
5–75	1
18–138	1
80–120	2
100–120	7
70–120	1
155–160	1
140	1
155	4

Reichhold Chemicals, Inc.

from final strength. The time required for development of strength by means of tack is very short compared to the time allowed for development of maximum strength. The measurement of tack of a pressure sensitive tape or label when the adhesive is applied to a surface without applied pressure and then immediately removed is known as *quick stick.*

Tack is a function of the rheological properties of the adhesive as well as the surface energy characteristics of the adhesive and the bonded surface. Resins modify both the rheological properties and surface energy of the adhesive formulation to give the proper flow and wetting characteristics. Tack is sensitive to variations in temperature, pressure, rate of application and removal of pressure, and contact time.

Adhesive strength refers to the strength of the bond produced by contact of an adhesive to a surface. Again, this ultimate strength will depend on temperature, pressure of application, and time of contact. Adhesion of pressure sensitive adhesives is usually measure by a peel test.

Cohesive strength refers to the internal strength of an adhesive or the ability of the adhesive to resist splitting. The clean peel of an adhesive from a surface requires that the cohesive strength of the adhesive be greater than the adhesive strength to the bonded surface. Unlike tack and adhesion, which are dependent on the surface being bonded, cohesive strength is not influenced by the substrate.

Tackifier Function

Tackifying resins enhance the adhesion of nonpolar elastomers by improving wettability, increasing polarity, and altering the viscoelastic properties of the adhesive mass. The understanding of how resins modify the viscoelastic properties of elastomers has developed significantly since the later 1960s. In 1966, C. Dahlquist[2] defined the performance of pressure sensitive adhesives on the basis of creep compliance. Sherriff, Aubrey, and co-workers[3] later demonstrated the effect of adding low molecular weight resins to natural rubber and examined the relationship between viscoelasticity and peel adhesion of rubber-resin blends.

More recently, Class and Chu[4] extended the use of dynamic mechanical measurements to a systematic study of resin-elastomer blends which revealed the relationship between the structure, concentration and molecular weight of resins and their effect on the viscoelastic properties of elastomers. Dynamic mechanical data typical of that obtained from an elastomer or elastomer-resin blend is shown in Fig. 4. G' is the elastic or storage modulus, G'' is the viscous or loss modulus, and the ratio of G''/G' gives the tan δ curve. The temperature at which the tan δ curve shows a maximum corresponds to a dynamic glass transition temperature. Class and Chu showed that with these types of measurements, the effect of modifying resins on the viscoelastic properties of elastomers can be readily determined. Resins which are compatible with an elastomer will cause a decrease in the elastic modulus G' at room temperature and an increase in the tan delta peak or glass transition temperature. Resins which are incompatible with an elastomer will cause an increase in the elastic modulus G' at room temperature and will show two distinct maxima in the tan delta curve.

Chu has also characterized numerous commercial pressure sensitive adhesives and shown that elastic modulus and glass transition temperature are key viscoelastic properties in characterizing pressure sensitive adhesive performance. An excellent review outlining the characterization of pressure sensitive adhesive by dynamic mechanical measurements and discussing how these data can aid in the formulating of adhesives has been recently published by Chu.[5]

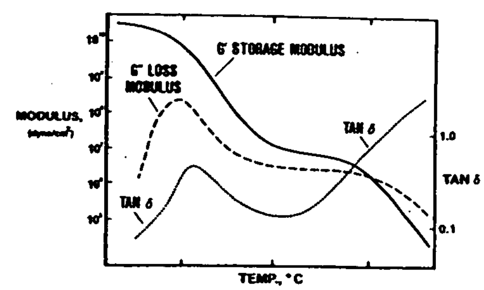

Fig. 4. Viscoelastic properties of polymers.

Tackifier Sel ction

The major factors which determine the utility of a resin as a tackifier are:

1. Chemical structure;
2. Molecular weight; and
3. Molecular weight distribution.

Other factors of importance are:

1. Softening point;
2. Initial color;
3. Color stability when heated; and
4. Oxidative and UV stability.

The modification of an elastomer by a low molecular weight resin is determined by the compatibility (or solubility) of the resin in the elastomer. Compatibility is necessary for generating tack, but compatibility does not insure that the desired adhesive properties will be obtained. Rheology studies have shown that adhesive performance is related to the elastic modulus at application temperature and to the glass transition temperature of the resin-elastomer blend. A tackifying resin has a glass transition temperature higher than that of an elastomer. The glass transition temperature of the resin-elastomer blend will thus increase as the level of resin is increased. The decrease in the elastic modulus will be determined by the compatibility of the resin with the elastomer. Thus, a formulator may be working with a compatible resin-elastomer blends but only certain combinations will allow him to obtain the desired level of elastic modulus and glass transition temperature.

An adhesive formulator has limitations on the amount of resin which can be incorporated into an elastomer in an attempt to obtain the desired combination of rheological properties. All resin-elastomer blends show a variation in adhesive properties vs. the concentration of resin. Fig. 5 shows probe tack as a function of resin concentration for a natural rubber-resin ester blend. This type of resin response curve is typical of all adhesive systems. In Fig. 5, little enhancement of tack is seen up to 40% resin concentration. Between 40 and 65% resin, there is a rapid increase in tack, followed by an equally rapid drop off in tack above 65% resin. Above, 65%, the system becomes overloaded in resin, incompatibility develops, and tack drops. The maximum in a resin response curve will be determined by the general compatibility

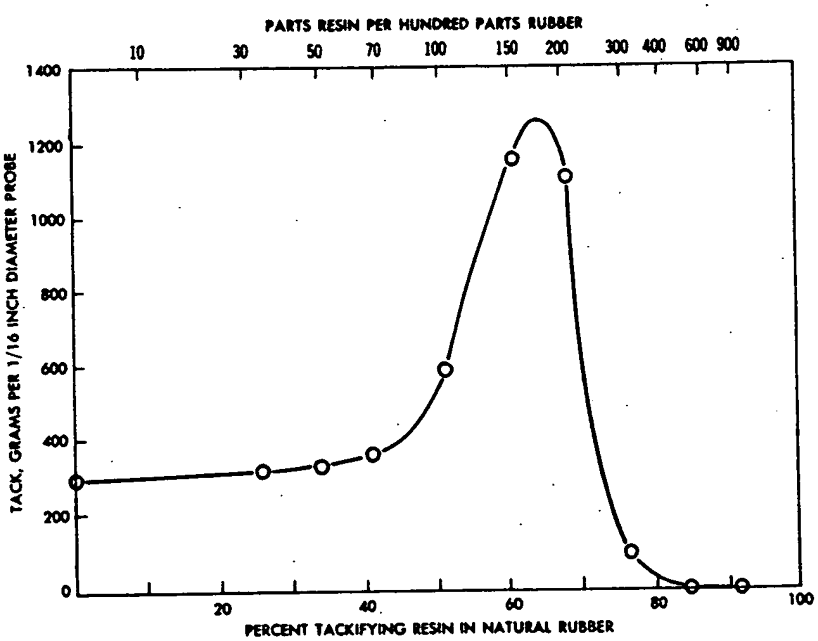

Fig. 5. Probe tack vs. resin concentration for natural rubber–rosin ester blend.

of the resin with the elastomer. Typically, the lower softening point versions of chemically similar resins will develop maxima at higher resin loadings than the higher softening point resins.

A simple test of compatibility is the clarity of a resin-elastomer blend. A 1 : 1 blend can be prepared in solution and cast onto a glass plate. The solvent is allowed to evaporate and the cast film observed for clarity. A clear film indicates good compatibility while a cloudy or opaque film indicates some degree of incompatibility.

A more quantitative indication of compatibility can be obtained with solvent or hot melt cloud point tests. The solvent cloud point tests are based on the idea that resins will be compatible with elastomers of similar chemical nature. Thus aliphatic resins will be effective tackifiers for aliphatic elastomers such as natural rubber, while aromatic resins are needed for aromatic elastomers such as SBR. Some resins, e.g., rosin esters, will be compatible with many different types of elastomers. Solvent cloud point tests are carried out in three solvent systems which represent aliphatic, aromatic, and polar systems. The solvent blends used by Hercules are:

1. Odorless mineral spirits (OMS), an aliphatic solvent;
2. Diacetone alcohol/xylene (DACP), a polar blend; and
3. Methylcyclohexane/aniline (MMAP), an aromatic blend.

The resin is dissolved in the test solvent either at room temperature or at elevated temperature. The solution is then cooled and the temperatures at which an initial and full cloud appears are recorded. Low cloud points indicate good solubility in that solvent type and predict good solubility of that resin in elastomers of the same chemical nature. As a rule of thumb, cloud points greater than 70°C indicate poor compatibility while cloud points less than 0°C indicate excellent compatibility. Table 2 shows cloud points for four types of resins—rosin esters (Staybelite 10 Ester and Foral 85, 105), pure monomer aromatics (Piccotex), polyterpene resin (Piccolyte), and C-5 aliphatic resins (Piccopale, Piccotac). The low cloud points of the rosin esters in all blends predicts that rosin esters would have wide compatibility with most elastomers—a fact that is well known. The other resins show more selectivity. The high cloud points in the polar and aromatic solvent blends in conjunction with a low OMS cloud point explains why C-5 aliphatic resins are compatible only with aliphatic elastomers such as natural rubber and the isoprene midblock of the styrene-isoprene-styrene block copolymer. Hot melt cloud point test can also be carried out with resin/polymer blends.

Table 2. Resin Cloud Points.

Resin	DACP, °C (Polar solvent)	MMAP, °C (aromatic)	OMSCP, °C (aliphatic solvent)
Staybelite 10 ester	<0	<0	< −10
Foral 85	<0	2	< −10
Foral 105	<0	15	< −10
Piccotex 120	<0	10	60
Piccotex 75	<0	0	−22
Piccolyte S-115	56	87	< −10
Piccolyte S-135	61	95	< −10
Piccopale® 100	70	97	10
Piccotac B	55	90	< −10

The choice of resin tackifier influences not only the initial adhesive performance, but also the retention of adhesive properties upon aging. Color retention and resistance to oxidation and UV degradation are key considerations in choosing a tackifying resin. Glycerine or pentaerythritol esters of unmodified wood rosin exhibit fair tack properties initially, but have poor aging characteristics primarily because of resin oxidation. Esters of rosins which have been stabilized by hydrogenation or polymerization, e.g., Foral 85 or Foral 105, possess the best combination of properties for adhesive use.

The stability of hydrocarbon resins varies greatly depending on chemical structure. Residual unsaturation in the resin molecule is the point for oxidative attack. Aliphatic C-5 resins and terpene resins can be protected with antioxidants to give good aging characteristics. Aromatic resins vary considerably in structure, but generally show good oxidative resistance. The most stable modifying resins available are those classified as hydrogenated resins. These resins are the result of hydrogenating aromatic,

aliphatic, or cycloaliphatic resins to remove as much unsaturation as possible. The water-clear initial color and color stability under oxidative, UV, and elevated temperature conditions make these the resins of choice for high-performance applications.

The development of the styrenic block copolymers has created special challenges for resin manufacturers. These block copolymers are of two basic types. The first are the *triblock copolymers*, consisting of an elastomeric midblock and thermoplastic polystyrene endblocks. These can be either the linear triblock copolymers, such as the Kraton polymers from Shell Chemical Company or the Europrene polymers from Enichem, or radial block copolymers, initially produced by Phillips Petroleum and now available from Petrofine SA under the tradename Finaprene. The linear triblock copolymers are the most widely used in the adhesive industry.

The second type of polymer is the *multiblock copolymer* based on styrene and butadiene, available from Firestone Synthetic Rubber and Latex Company under the tradename Stereon. This material has a much higher level of styrene than do the triblock copolymers (43% vs. 30% max.), but the formulation techniques used with this material would be similar to those used to compound a styrene-butadiene triblock copolymer.

Block copolymers, like most elastomers, require modifying resins to develop the desired adhesive properties. Tack is built into the formulation by the use of midblock associating resins, while enhanced thermal resistance and strength properties can be obtained by the use of endblock associating resins. The challenge to resins suppliers has been to design resins that will associate exclusively with the desired phase. Resins that associate with both phases are desired in some cases, and they can be effective tackifiers, but they typically cause a severe loss in the cohesive strength of the formulation. Table 3 lists modifying resins for block copolymers.

Table 4 shows the effect of molecular weight and molecular weight distribution on the tackifying effectiveness of three C-5 aliphatic resins. These three resins have softening points in the range of 92–100°C. Based on chemical structure, all three of these resins should be compatible with the isoprene midblock of a styrene-isoprene-styrene block copolymer. Piccopale 100, with the highest molecular weight and broadest molecular weight distribution, generates poor adhesive properties. Piccotac B, intermediate in molecular weight and molecular weight distribution, generates reasonable properties, while Piccotac 95, with the lowest molecular weight and narrowest molecular weight distribution, generates maximum adhesive properties. These data thus show that in a homologous series of resins, the lowest molecular weight resin with the narrowest molecular weight distribution generates optimum tack properties. There may be, however, other considerations such as optimizing shear resistance in a pressure sensitive adhesive that would cause a formulator to choose a resin that does not give optimum tack.

Table 3. Modifying Resins for Block Copolymers.

A. Midblock Tackifiers:
- Rosin esters
- Aliphatic C-5 hydrocarbon resins
- Terpene resins
- Aromatic-modified aliphatic resins
- Hydrogenated resins

B. Endblock Compatible Resins:
- Rosin esters
- Aromatic resins
- Low molecular weight resins

C. Endblock Reinforcing Resins:
- High softening point aromatic resins

Table 4. Adhesive Performance—Effect of Mw and MWD.

SIS	100	100	100
Piccotac® 95	100		
Piccotac® B		100	
Piccopale® 100			100
Quick Stick, oz/in.	66	38	1
180° Peel, oz/in.	105	80	35
Shear resistance, (min)	10,000+	10,000+	—
SAFT, °C	105	105	—

LATEX-BASED PRESSURE SENSITIVE ADHESIVES

It has been previously mentioned that government restrictions on the use of organic solvents

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If you have not already received Material Safety Data Sheets (MSDS) for these products, they will be sent to you upon request. All users of these products are urged to obtain and retain a copy of the MSDS and to study and use the information in the MSDS.

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SUPPORT PLASTICS RECYCLING

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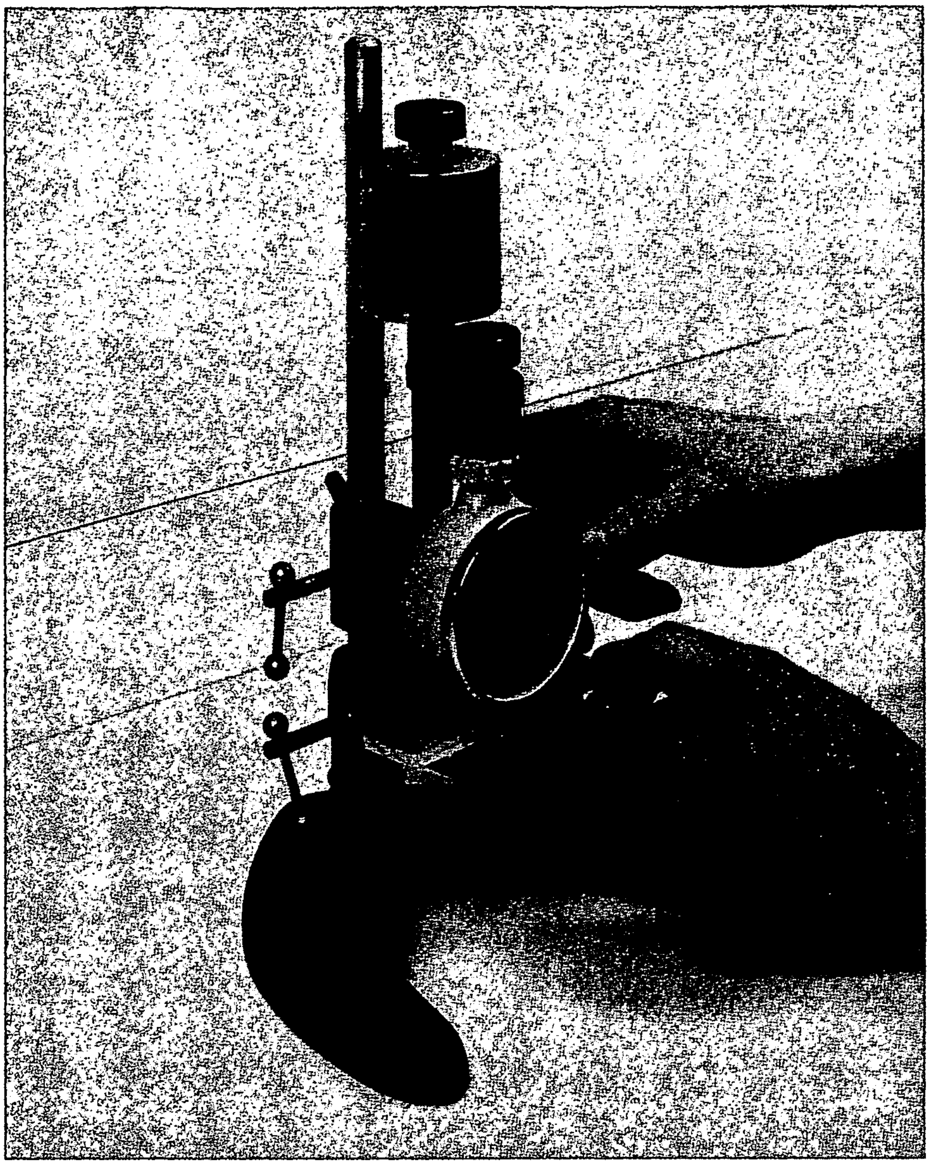

Figure 12. The hardness of a resin is measured with Shore Durometer. This instrument indicates on a dial how far a steel indentor penetrates into the specimen.

tation by a blunted needle, using an adjustable device **(Figure 12)** called a Shore Durometer (ASTM D 2240). The more flexible range A scale is used for EVA copolymers, while LDPE is more commonly reported in the higher range D scale. The softer polyolefins, i.e. those with low hardness values, are those with low crystallinities and high melt indices.

Softening Point

The ring and ball softening point (ASTM E 28) is the temperature at which a molded polymer disk becomes soft enough that the weight of a small steel ball causes it to sag one inch **(Figure 13)**. The disk is supported in a brass shoulder ring immersed in a heated water or oil bath. The temperature is raised at a rate of 5°C/minute.

The softening point of a polymer is important in hot melt adhesives because this property influences heat resistance, blocking point, application temperature and open time or solidification point. As can be seen from **Figure 14**, the ring and ball softening point is primarily dependent upon the melt viscosity or melt index of the polymer. Crystallinity has only a minor influence.

Hot Melt Adhesives

A hot melt adhesive is a thermoplastic material which is solid at room temperature. This adhesive can be applied in a molten form and adheres to a surface when cooled to a temperature below its melting point. Hot melt adhesives, as distinguished from hot melt coatings, are used to join two substrates together.

Hot melt adhesives differ from other liquids or hot applied systems in that they set by cooling rather than by chemical curing or by evaporation of a liquid carrier. The cooling produces rapid bonding. In addition, hot melt adhesives can be reused simply by reheating, can be formulated to bond with a wide variety of substrates and perform a gap-filling function. Hot melt adhesives have excellent moisture resistance and, because they are 100% solid, transportation and storage problems are minimized and energy costs are low.

In spite of their many advantages, hot melt adhesives do have some limitations. Because they are thermoplastic materials, heat resistance can be poor, particularly with EVA formulations. Additionally,

the strength of hot melt adhesives does not match that of thermosetting adhesives. Also, hot melt adhesives tend to produce surface bonds with less substrate penetration than solvent-borne adhesives.

However, the fact that they bond almost instantaneously makes hot melt adhesives useful for high speed packaging applications. The major market for hot melt adhesives is packaging, including case sealing, bag side seaming and end closing, tray forming, labels, folding cartons and composite cans. Other uses are in bookbinding, furniture edgebanding, textiles, shoe construction and automotive applications.

A typical hot melt adhesive is composed of three components:

- polymer
- tackifying resin
- wax

The polymer forms the backbone of the adhesive, controlling its strength and toughness. The tackifying resin contributes wetting and tack. The wax is used to lower the melt viscosity and control the setting speed. Antioxidants, fillers, plasticizers and blowing agents can also be used to enhance certain properties.

Backbone polymers used in hot melt adhesives include EVA copolymers, LDPE, amorphous polypropylene (APP), ethylene ethyl acrylate copolymers (EEA), polyamides, polyesters and thermoplastic elastomers (TPE). EVA copolymers are the most widely used polymers for hot melt adhesives because they are, as discussed earlier, compatible with both amorphous tackifying resins and crystalline waxes.

The backbone polymer is normally modified with a low molecular weight, non-crystalline, polymeric material known as a tackifying resin. Tackifying resins are derived from rosin or natural terpenes, or are synthesized from hydrocarbons.

Tackifying resins range from hard, brittle materials to semi-liquids. They are selected on the basis of their chemical polarity, softening point, heat stability and color. Tackifying resins can range from nonpolar, aliphatic hydrocarbons to highly polar, rosin esters. Polarity in tackifying resins affects substrate adhesion, polymer compatibility and, to a lesser extent, flexibility and adhesive viscosity.

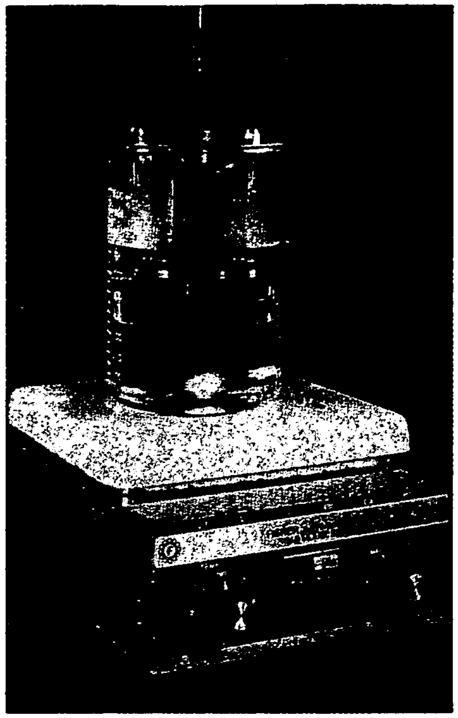

Figure 13. Ring and ball softening point apparatus

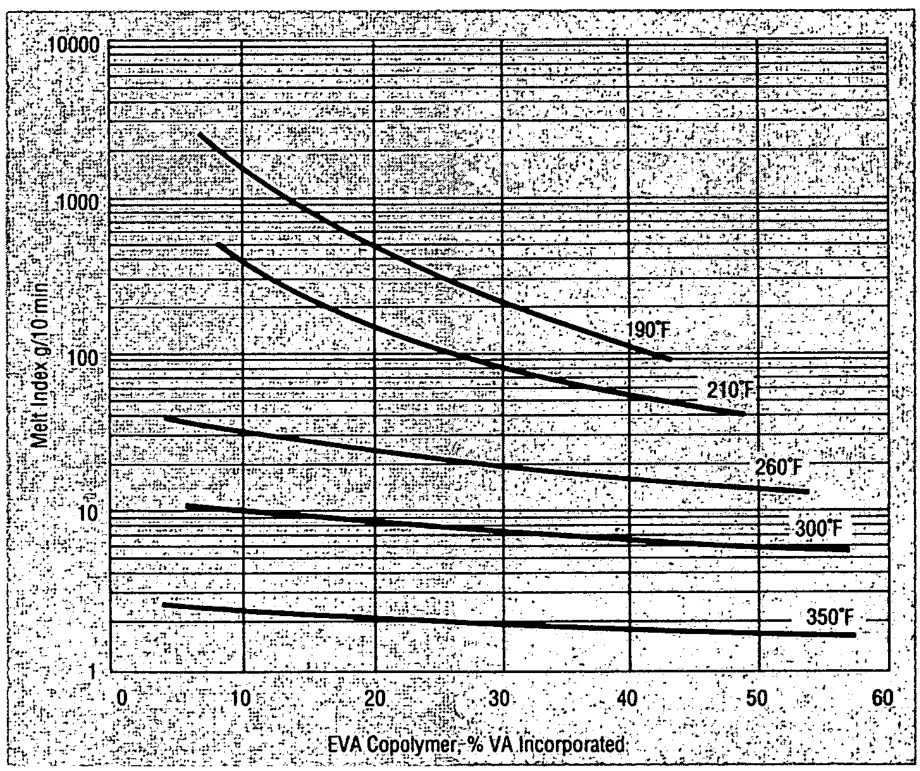

Figure 14. Ring and ball softening point for EVA copolymers (ASTM E 28).

Table 1: Effect of polymer properties on hot melt adhesive performance

		Cohesive Strength	Good Adhesion	Low Viscosity	Heat Resistance	Hot Tack (Melt Strength)	Flexibility	Short Set Time	Heat Stability
EVA	high VA	•					•		
	low VA		•		•			•	•
	high MI	•		•					
	low MI		•			•	•	•	•
LDPE	high Den		•		•			•	•
	low Den	•					•		
	high MI	•		•					
	low MI		•			•	•		

Table 2a: Hot melt adhesive properties as a function of VA incorporated. (EVA/hydrocarbon resin/paraffin wax @ 1:1:1 ratio)

ULTRATHENE Copolymer	UE 637 3 MI 9% VA Inc.	UE 645 3 MI 28% VA Inc.
Viscosity, cP @ 350°F	10,000	13,000
Ring and Ball Softening, °F	199	174
Tensile Strength, psi	900	710
Elongation, %	<10	93

Table 2b: Hot melt adhesive properties as a function of ULTRATHENE EVA MI in EVA/tackified wax system @ 1:1:1 tackifier: mixed hydrocarbon

ULTRATHENE Copolymer	UE 645 3 MI 28% VA Inc.	UE 653 388 MI 28% VA Inc.	UE 647 980 MI 28% VA Inc.
Viscosity, cP @ 350°F	9,500	330	200
Ring and Ball Softening Point, °F	170	164	158
Tensile Strength, psi	950	350	340
Elongation, %	560	40	40
Hardness, Shore A, original	Max 87	Max 91	Max 84
after 15 sec.	84	83	80
SAFT,* °F	158	148.1	148.1

*SAFT – Shear Adhesion Failure Temperature (ASTM D 4498)

property can seldom be obtained without affecting some other important adhesive property. Therefore, formulating an adhesive to meet a specific set of requirements involves a series of trade-offs and compromises and is typically an empirical process of preparing a batch and then testing its adhesive properties. This trial and error approach can be simplified with a basic understanding of the effect of the different polymer properties on adhesive performance and the relationship of these properties to other hot melt adhesive components.

Selecting the Polymer

The polymer is the single most important component of a hot melt adhesive. It is the backbone of the adhesive, the major factor controlling cohesive strength, flexibility, viscosity, heat resistance and hot tack (melt strength).

Performance properties of hot melt adhesives are listed at the top of **Table 1.** The factors that must be considered in selecting an ULTRATHENE or PETROTHENE polymer for hot melt adhesives are listed on the left side. A solid dot indicates which polymer variable is the best choice to improve the specific adhesive property. Some of the inherent trade-offs are apparent, as for example, the effect of melt index on viscosity and hot tack.

Table 2a shows the effect of two ULTRATHENE copolymers, differing in VA incorporated, on the properties of formulated hot melt adhesives. The tackifying resin and wax are the same in each formulation. The tackifying resin is a medium molecular weight, hydrogenated, aliphatic hydrocarbon with a softening point of 100°C (212°F). The fully refined paraffin wax has a melting point of 68°C (155°F).

A comparison of the formulation containing ULTRATHENE UE 637 to the ULTRATHENE UE 645 blend shows the effect of higher VA incorporated on the final adhesive. The adhesive with less VA incorporated in its polymer is stronger, but more brittle and has a higher softening point.

Table 2b shows the effect of different ULTRATHENE copolymers with the same VA incorporated but differing in melt index. Again, the tackifying resin and wax are the same in each formulation. The higher melt index EVA produces lower viscosity at the expense of strength and flexibility.

Table 4: Hot melt adhesive properties as a function of wax type

Wax Type	Paraffin Wax (155°F MP)	Microwax (163°F MP)	Synthetic Wax (217°F MP)
Viscosity, cP @ 300°F	615	875	850
Ring and Ball Softening Point °F	164	181	229
Tensile Strength, psi	350	170	280
Elongation, %	40	30	20

For high VA incorporated, less crystalline ULTRATHENE and VYNATHENE copolymers, cloud point temperature is less meaningful. The compatibility of esters, aromatic hydrocarbons and low molecular weight, styrene resins tend to increase with increasing polymer VA incorporated. This increase is due to the affinity of these tackifiers for the acetate functional groups more prevalent in the higher VA incorporated copolymers.

Natural polyterpenes and aliphatic hydrocarbons, on the other hand, generally are more compatible with the polymers of high ethylene content and lower VA incorporated

Selecting the Tackifying Resin

The tackifier improves the adhesion characteristics of the polymer, can enhance adhesion to specific substrates and can improve wetting by reducing adhesive viscosity. Hot tack and many other performance properties can also be improved by the tackifier.

Tackifying resins are selected on the basis of chemical composition or functionality, softening point, cost, initial color and heat stability. The variety of tackifying resins available for hot melt adhesives is quite extensive. Tackifiers range from viscous liquids to high melt point, hard thermoplastics. Tackifiers differ in functionality from nonpolar, aliphatic hydrocarbons to polar, ester resins. Their colors cross the spectrum from water-white to dark brown.

EVAs are most compatible with polar, aromatic hydrocarbon tackifying resins and rosin esters. These resin types include Zonester 85,* Sylvatac 1105,* Permalyn 105** and Foral 85.**

Selecting the Wax

The primary functions of a wax are to reduce viscosity, control open time and adjust the softening point of a hot melt adhesive. Petroleum and synthetic waxes are compatible with PETROTHENE LDPE and ULTRATHENE EVA copolymers up to 30% VA incorporated.

Waxes differ in melting points, melting point range and flexibility. The three major categories of waxes are paraffin, microcrystalline and synthetic. Paraffin waxes are widely used in hot melt coatings because of their excellent barrier properties. Microcrystalline waxes are more flexible and have better adhesive properties than paraffin types and normally have high melting points. For this reason, microcrystalline waxes are used for faster-setting adhesives. Waxes synthesized using the Fischer-Tropsch process are characterized by very high melt points and are used in adhesives where high temperature performance and fastest setting speeds are required.

Hot melt adhesive formulations containing a typical paraffin wax, microcrystalline wax and synthetic wax are compared in **Table 4**. Microcrystalline wax produces a more flexible adhesive, while synthetic waxes result in adhesives with the highest SAFT.

The relative melting point of the wax and the EVA can determine the adhesive

*Zonester and Sylvatec are registered trademarks of Arizona Chemical Co.

**Permalyn and Foral are registered trademarks of Hercules, Inc.